Critical Adsorption, Order-Parameter Profile, and Surface Tension: Theory Versus Experiment

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In the present work, we discuss the crossover behavior of the order parameter profile in simple fluids under critical and supercritical conditions. We develop a crossover theory for the critical adsorption profile, analogous to crossover theories for bulk critical phenomena in a simple fluid [1]. The crossover expressions are obtained to first order in ε within the RG approach proposed by Rudnick and Jasnow [2] for semi-infinite systems. The universal crossover function for the order-parameter profile is completely consistent with new Monte Carlo calculations on a three-dimensional Ising model [3] and in the asymptotic scaling regime corresponds to the Fisher-de Gennes hypothesis [4].

We test the theory against the surface excess (Gibbs) adsorption experimental data for CO_2/silicia [5] and SF_6/graphite [6] systems. On the non-critical isochores, good representation of experimental data is achieved in the range of temperatures from the saturated temperature up to 1.15Tc and densities $0.5\rho_c \leq \rho \leq 1.5\ \rho_c$. The optimization of the model to the excess isotherms in both systems indicates that they have surface critical behavior in the universality class of *normal* transitions. However, in this case the model does not reproduce the excess adsorption data along the critical isochore for SF_6/graphite system at dimensionless temperatures $\tau \leq 0.01$. Analysis of the excess adsorption data along the critical isochore in SF_6/graphite system indicates that the surface field h_1 vanishes linearly with τ as $T \rightarrow T_c$, which corresponds to the *ordinary* transition.

The crossover behavior of the surface tension in one-component fluids is also discussed. The crossover expression for the Sugden parameter was verified by direct comparison with the experimental data for Ar, O_2, CH_4, CO_2, C_5H_{12}, C_6H_{14}, C_7H_{16}, and C_8H_{18}.

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